

Differential EXAFS analysis using *DEXA*

M. P. Ruffoni

Received 12 December 2008

Accepted 25 May 2009

European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, 38043 Grenoble Cedex, France.

E-mail: ruffoni@esrf.fr

Differential EXAFS is a new XAS technique dedicated to directly measuring the tiny atomic displacements that arise from such strain-inducing phenomena as magnetostriction, piezoelectricity and thermal expansion. These new experiments have presented the need for new analysis tools to extract and quantify the measured atomic strains, a need that has been addressed by the development of the *DEXA* code.

© 2009 International Union of Crystallography
Printed in Singapore – all rights reserved

Keywords: *DEXA*; differential EXAFS; DiffEXAFS; DiffXAS.

1. Introduction

Established in 2005 by Pettifer *et al.* (2005), differential X-ray absorption spectroscopy (DiffXAS or DiffEXAFS when applied to the extended fine-structure region) is a new approach to dichroism studies that exploits the high-stability low-noise conditions found on third-generation X-ray spectroscopy beamlines, to measure tiny perturbations to atomic structures that are induced by the modulation of some external sample property (Ruffoni *et al.*, 2007a). The initial experiments were performed on ID24, the dispersive EXAFS beamline of the European Synchrotron Radiation Facility (ESRF) (Pascarelli *et al.*, 2006), and showed a sensitivity to mean atomic displacements of the order of femtometres when measuring the Joule magnetostriction of a thin film of ferromagnetic FeCo.

Since then, the technique has been extended to the study of thermally induced strains (Ruffoni *et al.*, 2007b; Ruffoni, 2007), whilst further magnetostriction measurements have revealed the atomic origins of strain enhancement in the technologically interesting FeGa system (Ruffoni *et al.*, 2008), and have proven to be an important tool for investigating magnetoelastic coupling in 3d metal alloys (Pascarelli *et al.*, 2007).

Naturally, this development process has involved the design of new experimental apparatus and data acquisition procedures, but, equally importantly, has included the production of a new analysis code for processing DiffEXAFS signals and extracting quantitative strain information. This code is the *Differential EXAFS Analyser (DEXA)*, which is presented here.

2. Concept

DEXA provides an environment in which to analyse DiffEXAFS signals and quantify the structural modifications observed within. In essence, it takes the results of *ab initio* EXAFS calculations obtained from the *FEFF* code (Ankudinov *et al.*, 1998), generates the corresponding DiffEXAFS signal for a given set of structural perturbation coefficients, and fits the resulting theory spectrum to experimental data.

As is consistent with the nature of DiffEXAFS, the first task in the analysis process is to define a reference structure from which the strains observed in the DiffEXAFS are measured. This can be obtained quite readily from one of the many standard EXAFS

Table 1

Some examples of sample properties that could be measured with DiffEXAFS, and the types of tensors associated with their behaviour.

Since strain is described by a second-rank tensor, the minimum rank of **T** must also be two.

Tensor rank	Variable rank	Sample property (variable)
Second	Zeroth (scalar)	Thermal expansion (temperature)
Third	First (vector)	Piezoelectricity (electric polarization)
Fourth	First × 2	Magnetostriction (magnetization)
Fourth	Second	Elasticity (stress)

analysis codes¹ by fitting the conventional EXAFS signal from the sample being studied. *DEXA* then takes the results from this fit, and, along with the photoelectron scattering phase and amplitude information from *FEFF*, generates a baseline EXAFS spectrum onto which the DiffEXAFS perturbations may be applied, and then fitted.

To date, the DiffEXAFS experiments conducted on ID24 have focused primarily on magnetostriction studies, a fact reflected in the development of *DEXA*. However, since DiffEXAFS spectra may, in principle, be taken from the modulation of any given sample property, *DEXA* employs a general approach to modelling atomic strain, one that is based on Cartesian tensors.

This essentially eliminates the need for any specific case-by-case information exclusive to the type of DiffEXAFS being undertaken. All that must be known is the rank of tensor, **T**, associated with the property under study. Some examples are given in Table 1, but, within this framework, any of them may be replaced with measurements of properties that possess the same tensor characteristics without need of any modifications to the fitting algorithm (*e.g.* replacing magnetostriction with electrostriction).

With these tensors, the strain, Δl , of any photoelectron scattering path leg is given by

$$\Delta l = \sum_{ij} \Delta \varepsilon_{ij} \beta_i \beta_j = \sum_{ij(N)} T_{ij(N)} \beta_i \beta_j (M'_{(N)} - M''_{(N)}), \quad (1)$$

where ε is the strain tensor, which gives Δl when contracted onto the leg vector β . On the right-hand side, **M** describes the modulated sample property, which is of rank *n*. These *n* dimensions then form

¹ Such as *FEFFIT* (Newville *et al.*, 1995), *EXCURV* (Binsted *et al.*, 1992; Binsted & Hasnain, 1996) or *GNXAS* (Di Cicco, 1995).

the set $\{N\}$, which, when added to the two dimensions of the strain tensor, gives the rank of \mathbf{T} . The two separate sample states used at the time of measurement are given by \mathbf{M}' and \mathbf{M}'' , and their difference defines the perturbations seen in the DiffEXAFS.

Summing the Δl contributions over all legs in a given scattering path, and remembering to account for the X-ray polarization dependence of the EXAFS (Pettifer *et al.*, 2005), gives Δs_j , the change in length of scattering path j as seen in the differential fine-structure function (Pettifer *et al.*, 2005),

$$\Delta\chi(k) = \sum_j A_j(k)k \cos[s_j k + \varphi_j(k)]\Delta s_j. \quad (2)$$

This representation of $\Delta\chi$ is based on a first-order Taylor expansion of the conventional EXAFS fine-structure function, using a real photoelectron wavevector, and neglecting the strain of s_j -dependent terms in $A_j(k)$. However, for greater accuracy in modelling DiffEXAFS spectra, *DEXA* relaxes these approximations.

Instead it calculates two full EXAFS spectra for the sample, one with and one without the DiffEXAFS perturbations applied, and then generates the DiffEXAFS signal explicitly from the difference between the two. These EXAFS spectra are constructed using the information in *FEFF*'s `feffnmmn.dat` files as described by equation (3) of Newville (2001).² Following the same definitions and nomenclature given by Newville (2001) (and noting that $s_j = 2R_j$, and that p is the complex wavevector), *DEXA* first groups the constant modulation-independent amplitude factors into a single function,

$$C_j(k) = \frac{S_{0j}^2 N_j F_j(k)}{k} \exp\left[\frac{-2R_j}{\lambda(k)} - 2p^2 \sigma_j^2\right]. \quad (3)$$

A similar function is then defined for those factors that do vary between measurements at \mathbf{M}' and \mathbf{M}'' ,

$$D_j(\Delta R_j) = \frac{1}{(\Delta R_j + R_j)^2}. \quad (4)$$

Note here that ΔR_j is the first cumulant for consistency with Newville. The DiffEXAFS strains will later be defined as Δr_j . Finally, *DEXA* calculates a function for the scattering phase,

$$\Phi_j(k, \Delta R_j) = 2kR_j + \delta_j(k) + 2p\Delta R_j - \frac{4p\sigma_j^2}{R_j}. \quad (5)$$

S_{0j}^2 , ΔR_j , σ_j^2 and possibly N_j are provided to *DEXA* following a conventional EXAFS analysis of the sample. All the other terms in equations (3) to (5) are calculated *ab initio* from a model structure supplied to *FEFF*.

This information is then used to construct $\chi'(k)$ and $\chi''(k)$, the EXAFS at each of the two sample states, and their difference calculated to give $\Delta\chi(k)$,

$$\Delta\chi(k) = \sum_j C_j(k) [D_j(\Delta R_j) \sin \Phi_j(k, \Delta R_j) - D_j(\Delta R_j + \Delta r_j) \sin \Phi_j(k, \Delta R_j + \Delta r_j)]. \quad (6)$$

A comparison between this explicit difference formalism and that of the Taylor expansion given by equation (2) can be seen in Fig. 1. Both deviate from a model spectrum at low k since *DEXA*'s calculations are not valid in the near-edge region. In the EXAFS region, equation (6) is the better of the two, though both reproduce the model signal to within 1% of its amplitude. Neither reproduce the *FEFF* result exactly, since the scattering phases and amplitudes are not recalculated between $\chi'(k)$ and $\chi''(k)$.

To obtain the strains in a real system, it is necessary to find all the elements of \mathbf{T} in (1). This can be problematic when \mathbf{T} has a high rank,

² The third and fourth cumulants are neglected.

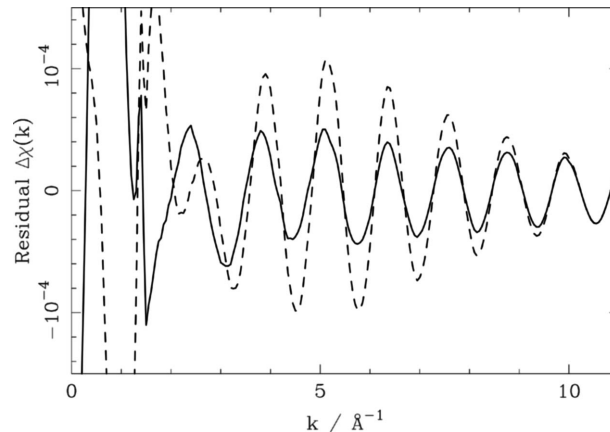


Figure 1

The differences between a model *FEFF* calculation and *DEXA* calculations using the explicit difference (solid line) and Taylor expansion (dashed line) formalisms in the k -range commonly measured on ID24. The explicit difference formalism yields smaller residuals, though in absolute terms each plot is less than 1% of the model spectrum amplitude. The model consisted of three Fe atoms spaced equidistantly at 3 Å intervals along a line parallel to the presumed X-ray polarization vector \mathbf{P} (a spacing comparable with the Fe lattice parameter). The central atom was taken to be the absorbing atom, with the outer two then forming a single scattering shell. Three calculations were performed with *FEFF*: one for the unstrained case, one for a strain of 1000 p.p.m. parallel to \mathbf{P} , and one for a 1000 p.p.m. strain perpendicular to \mathbf{P} . The difference between these last two spectra gave the model DiffEXAFS. The information from the unstrained case was supplied to *DEXA* as a reference structure.

and more so if the sample structure has little symmetry. A typical DiffEXAFS spectrum obtained on ID24, and Fourier-filtered to extract contributions from just a few scattering paths, will contain enough information to fit between four and six parameters, considerably fewer than the possible 81 tensor elements of a fourth-rank property such as magnetostriction.

However, the number of independent elements in \mathbf{T} may be reduced through Neumann's Principle (Nye, 1985) with knowledge of the point group symmetry of the crystal under study. Averaging effects can also be considered when dealing with amorphous or disordered samples. In the case of cubic crystals, for instance, just two parameters are necessary: one to describe strain in the [100] direction, and one for strain in the [111] direction. *DEXA* therefore allows the crystal symmetry to be specified (which includes 'isotropic' for non-crystalline samples) and will then construct \mathbf{T} from the subsequently reduced set of coefficients.

In addition to this, it is important to remember that, locally, strain may deviate from some single average value obtained for the sample as a whole. This is particularly true if the sample contains more than one atomic species. *DEXA* does not, therefore, limit the DiffEXAFS calculation to just one \mathbf{T} for all scattering paths. Instead, the sample may be split into 'substructures' and each assigned its own \mathbf{T} .

Take a binary system AB at an A absorption edge, for example. One set of parameters may be used to calculate \mathbf{T}_A for bonds of type $A-A$, and another set to make \mathbf{T}_B for bonds of type $A-B$. There are no restrictions as to how a structure is decomposed in this way, as long as the total number of fit parameters does not exceed the number of independent points in the experimental spectrum.

One final situation to consider is that posed by polycrystalline samples. Equation (6) describes the strain developed by a single crystal or crystallite based upon its orientation with respect to \mathbf{P} (the X-ray polarization vector), \mathbf{M}' , \mathbf{M}'' and the direction of beam propagation. To model the DiffEXAFS for a polycrystalline sample, *DEXA* solves (6) for multiple crystallite orientations and performs a configurational average of the results. This must take into consid-

eration the real distribution of crystallites within the sample, such as whether or not any preferential orientations exist and, if so, what fraction of the total number of crystallites are orientated as such.

The complete fitting prescription is therefore as follows.

(i) Establish all the modulation independent factors in (6) from a combination of *ab initio* calculation and conventional EXAFS fitting. Once loaded into *DEXA*, these define the sample reference structure, from which the perturbations seen in the DiffEXAFS are measured.

(ii) Declare basic information concerning the geometry of the sample. This includes its orientation with respect to \mathbf{P} , \mathbf{M}' , \mathbf{M}'' and the direction of beam propagation, and the arrangement and distribution of crystallites if it is polycrystalline. The type of sample must also be declared, and, if it is crystalline, its point group symmetry.

(iii) Contract \mathbf{T} onto each photoelectron scattering leg and sum the contributions to obtain Δr_j for each full path. Then equation (6) is solved to obtain the differential fine-structure, $\Delta\chi(k)$.

(iv) Compare the calculated $\Delta\chi(k)$ with that obtained experimentally, modify the fitted parameters in an attempt to reduce the differences between theory and experiment, and iterate until no further improvements can be made.

3. Interface

Fitting DiffEXAFS, as with conventional EXAFS, can be a subtle process based on trial and error. It is therefore important that it be approached in a systematic way. For that reason, *DEXA* fits DiffEXAFS spectra according to instructions in an input script. This script must prepare the fit environment, as described in the previous section, and then indicate which parameters should be fitted to the experimental DiffEXAFS.

Such an interface, which executes commands in a simple sequential fashion, has been selected over, for example, a graphical interface, since it is easier to see exactly how *DEXA* will approach the analysis of a given DiffEXAFS spectrum. This clarity is retained for both simple analyses, requiring just a few commands, or for complex larger scripts potentially involving the analysis of a number of spectra simultaneously. It also provides a means to quickly modify a fit, and ensures a clear record of a given fit is maintained. Multiple experimental spectra may also be analysed in a consistent fashion simply by distributing one script between them.

A full description of all the valid script commands, along with examples for their usage, is given in the manual accompanying the *DEXA* package. Fig. 2 shows an example of a typical script that might be used for the analysis of a magnetostrictive DiffEXAFS spectrum in order to show the usage of the most important commands.

The configuration of the sample environment at the time of measurement is typically given first. In the case shown here, \mathbf{M}' and \mathbf{M}'' are defined as two sample magnetization vectors, (x_1, y_1, z_1) and (x_2, y_2, z_2) , which are set with the magnetization command. The X-ray polarization vector (x, y, z) is then defined with the polarization command. All three vectors are unit vectors given with respect to the beamline frame, where $+x$ is horizontal towards the storage ring, $+y$ is vertical from the floor up, and $+z$ is the direction of beam propagation.

Assuming the sample under study is not amorphous, it is also necessary to use *preorientation* to define the one or more rotations that are required to orientate the sample crystallites correctly within the beamline frame. In the case of a single crystal, for example, one rotation alone is sufficient: $(\theta_1, \theta_2, \theta_3)$ in radians about x, y, z , respectively, from the nominal orientation of the atomic cluster

```

-----
* DEXA Execution Script
-----
* Define the Spectrum object
*
magnetisation 1 0 0 0 1 0
polarisation 1 0 0
preorientation 0 0 0 1.0

create FeSpectrum

FeSpectrum.spectrum FeDiffEXAFS.dat 0 1 2
FeSpectrum.feffinp feff.inp
FeSpectrum.pathsdat paths.dat
FeSpectrum.filter 3.0 10.0 1.0 2.0 3.0 0.2

FeSpectrum.addpath feff0001.dat
FeSpectrum.addpath feff0002.dat

-----
* Insert the EXAFS fit results
*
FeSpectrum.updatepath feff0001.dat S02 0.80
FeSpectrum.updatepath feff0002.dat S02 0.80
FeSpectrum.updatepath feff0001.dat Sig2 0.003
FeSpectrum.updatepath feff0002.dat Sig2 0.004
FeSpectrum.updatepath feff0001.dat dR 0.01
FeSpectrum.updatepath feff0002.dat dR 0.02
FeSpectrum.setparameter dE 1.0

-----
* Declare the fit parameters
*
FeSpectrum.symmetry cubic
FeSpectrum.fitparameter lg2 lambdaG2
FeSpectrum.fitparameter le2 lambdaE2

-----
* Start the fit and save the results
*
FeSpectrum.setparameter lambdaG2 1e-4
FeSpectrum.setparameter lambdaE2 5e-5
FeSpectrum.savespectrum FirstGuess.dat

startfit
saveparams Parameters.dat
FeSpectrum.savespectrum FeSpectrumFit.dat

```

Figure 2

An example of a typical script that might be used for the analysis of a magnetostrictive DiffEXAFS spectrum in order to show the usage of the most important commands.

in *FEFF's* *feff.inp* to the orientation in which the crystal was actually mounted during the experiment.

With the sample environment defined, it is then necessary to create at least one spectrum object with the *create* command and load the appropriate data into it. The experimental DiffEXAFS is specified with the *.spectrum* property, *FEFF's* *feff.inp* and *paths.dat* files *via* the *.feffinp* and *.pathsdat* properties, and all the scattering paths to be considered in the fit loaded from their *feffnnn.dat* files with *.addpath*. It may also be desirable to Fourier-filter the experimental DiffEXAFS prior to fitting, which can be done using a spectrum's *.filter* property. Currently, filtering is performed with a Hann window. This will then define everything needed to construct an *ab initio* DiffEXAFS spectrum.

It is then necessary to refine *FEFF's* parameters by inserting the results from a conventional EXAFS fit (performed for the same

FEFF calculation). `.updatepath` may be used to modify the properties of specific scattering paths, or `.setparameter` when changing a globally applied parameter. `.setparameter` may also be used to define a first guess to the optimization of the *DEXA* fit parameters.

With the DiffEXAFS theory spectra fully defined, `.fitparameter` is used to instruct *DEXA* to fit specific parameters. The names of these vary depending on the system under study. For magnetostriction in a cubic system, as shown here, `lambdaG2` and `lambdaE2` refer to the λ^{γ^2} and λ^{ϵ^2} coefficients, respectively (de Lacheisserie, 1993). If multiple spectra are being considered within a single execution of *DEXA*, parameters that affect more than one spectrum may be linked by assigning them the same name. For instance, entering

```
FeSpectrum.fitparameter lg2 lambdaG2
CoSpectrum.fitparameter lg2 lambdaG2
```

will cause a single parameter, named `lg2`, to be fitted to the λ^{γ^2} property of both `FeSpectrum` and `CoSpectrum`.

Finally, `startfit` is called to initiate the fit, with `saveparams` and `.savespectrum` also being called, either before or after this command, to save *DEXA*'s initial or optimized states, respectively.

4. Summary

DEXA has been used to analyse magnetostrictive DiffEXAFS data sets acquired from various materials measured on ID24 at the ESRF. Most notable amongst these are recent measurements on the technologically important $\text{Fe}_{(1-x)}\text{Ga}_x$ system, which revealed the atomic origins of the strain enhancement observed when Ga atoms are inserted into the Fe lattice (Ruffoni *et al.*, 2008). Further results will be published elsewhere shortly.

Since DiffEXAFS is a technique that is constantly expanding and diversifying into new areas with time, *DEXA* must also develop in a similar fashion. To aid this, the *DEXA* code has been written in a modular style with cross-platform compatible C++, enabling it to be easily built upon or modified in the future. The code is also available free of charge *via* SourceForge (<http://www.sourceforge.net/>) under

the terms of the GNU General Public License to enable users to make their own changes as necessary.

To date, the author has focused primarily on magnetostriction measurements and, as such, the greatest functionality exists when dealing with fourth-rank tensor properties in cubic or tetragonal systems. This will shortly be extended to permit analysis of systems of any symmetry, and of other types of DiffEXAFS measurements.

The author would like to thank S. Pascarelli and O. Mathon for their ongoing support for DiffEXAFS experiments on ID24 at the ESRF.

References

- Ankudinov, A. L., Ravel, B., Rehr, J. J. & Conradson, S. D. (1998). *Phys. Rev. B*, **58**, 7565–7576.
- Binsted, N. & Hasnain, S. S. (1996). *J. Synchrotron Rad.* **3**, 185–196.
- Binsted, N., Strange, R. W. & Hasnain, S. S. (1992). *Biochemistry*, **31**, 12117–12125.
- Di Cicco, A. (1995). *Physica B*, **209–209**, 125–128.
- Lacheisserie, E. d. T. de (1993). *Magnetostriction: Theory and Applications of Magnetoelasticity*, pp. 130–136. New York: CRC Press.
- Newville, M. (2001). *J. Synchrotron Rad.* **8**, 96–100.
- Newville, M., Ravel, B., Haskel, D., Rehr, J. J., Stern, E. A. & Yacoby, Y. (1995). *Physica B*, **208–209**, 154–155.
- Nye, J. F. (1985). *Physical Properties of Crystals: Their Representation by Tensors and Matrices*, pp. 20–24. Oxford University Press.
- Pascarelli, S., Mathon, O., Muñoz, M., Mairs, T. & Susini, J. (2006). *J. Synchrotron Rad.* **13**, 351–358.
- Pascarelli, S., Ruffoni, M. P., Trapananti, A., Mathon, O., Aquilanti, G., Ostanin, S., Staunton, J. B. & Pettifer, R. F. (2007). *Phys. Rev. Lett.* **99**, 237204.
- Pettifer, R. F., Mathon, O., Pascarelli, S., Cooke, M. D. & Gibbs, M. R. J. (2005). *Nature (London)*, **435**, 78–81.
- Ruffoni, M. P. (2007). PhD thesis, Warwick University, UK.
- Ruffoni, M. P., Pascarelli, S., Grössinger, R., Sato Turtelli, R., Bormio-Nunes, C. & Pettifer, R. F. (2008). *Phys. Rev. Lett.* **101**, 147202.
- Ruffoni, M. P., Pettifer, R. F., Pascarelli, S., Trapananti, A. & Mathon, O. (2007a). *13th International Conference on X-ray Absorption Fine Structure*, edited by B. Hedman, pp. 838–841. New York: American Institute of Physics.
- Ruffoni, M. P., Pettifer, R. F., Pascarelli, S., Trapananti, A. & Mathon, O. (2007b). *J. Synchrotron Rad.* **14**, 421–425.